

LA-UR-21-26289

Approved for public release; distribution is unlimited.

Title:	Geochemistry in support of LANL's national and energy security missions
Author(s):	Neil, Chelsea Wren
Intended for:	IMS Student Lecture Series presentation
Issued:	2021-07-02

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.



Geochemistry in support of LANL's national and energy security missions

Chelsea Neil, EES-14

July 13, 2021

IMS Student Lecture Series

Research Background

2006 – 2010

Tufts University

B.S., Chemical Engineering

2010 – 2016

Washington University in St. Louis

Ph.D., Energy, Environmental and Chemical Engineering

Dissertation: “Understanding the Nano- and Macro-scale Processes Impacting Arsenic Mobilization during Managed Aquifer Recharge”

2016 – 2018

U.S. Environmental Protection Agency

ORISE Postdoctoral Researcher

2018 – now

Los Alamos National Laboratory

Postdoctoral Research Associate (5/2018 – 6/2020)

Scientist 2 (6/2020 – present)



Chelsea Neil

cwneil@lanl.gov

505-695-3485

TA-48, Bldg. 0034, 115C

What is geochemistry?

- Field of science that uses **chemistry** to explain processes occurring within **geological systems**
- Can encompass interconnected fields of **geology**, **hydrology**, **biology**, and **atmospheric science** as they relate to natural processes in the environment

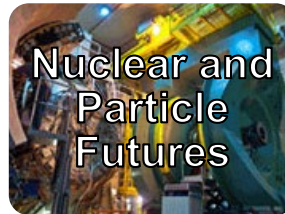
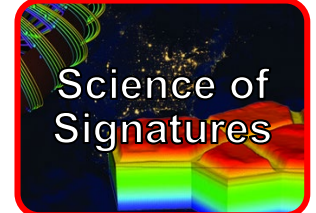


<https://www.sporcle.com/games/kjeverhart/pick-the-national-park-geology>

Why is geochemistry important?

- Geochemistry can play an important role in mission-critical LANL research areas:
 - Science of Signatures
 - Complex Natural and Engineered Systems

Los Alamos Capability Pillars



EES Strategic Themes and Focus Areas

EES Strategic Themes

Earth Science Solutions for Energy Security

- Subsurface Reservoir Signatures and Measurements
- Fractured Reservoir Modeling
- Controlling Flow in Subsurface Reservoirs



Earth System Science for Global Security

- Source Physics and Phenomenology
- Signal and Signature Propagation
- Detection and Monitoring
- Weapons Program Technology

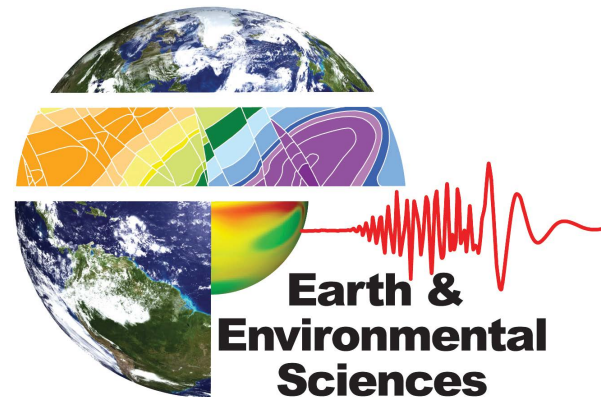


Earth System Dynamics and Impacts

- Regional Stability
- Environmental Surveillance
- High-Impact Environments

Earth Sciences in Support of the Nuclear Mission

- Repository Science
- Nuclear and Strategic Materials
- Legacy Environmental Contamination



Geochemistry for national and energy security missions

Earth Science Solutions for Energy Security

- Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)
- Investigating geologic carbon sequestration (GCS) in mafic/ultramafic rocks



Earth Science Solutions for Global Security

- Measuring transport and reactivity of semi-volatile xenon precursor, iodine, through geologic media
- Understanding the diffusive transport of noble gas signatures (xenon, krypton) in the subsurface



Earth Science Solutions for Energy Security

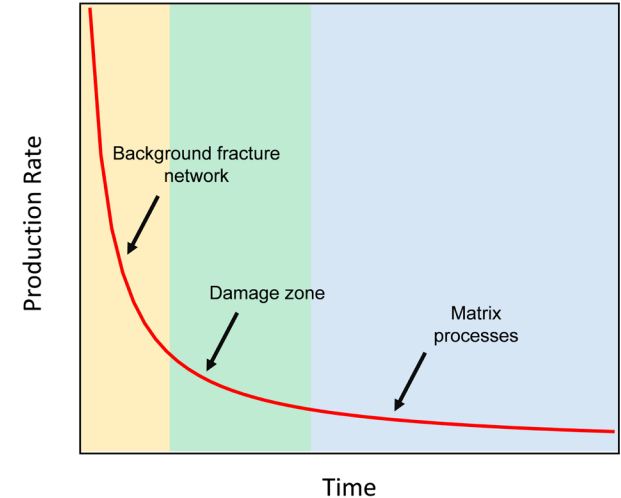
- Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)
- Investigating geologic carbon sequestration (GCS) in mafic/ultramafic rocks

Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Background/Motivation

- Low hydrocarbon recoveries in tight shale formations (<10% for oil; ~20% for gas)
 - Production rates decline rapidly within one year due to limited diffusion at smaller scales, especially within matrix nanopores.
- Conventional experimental techniques limited to measuring open pores (e.g. gas absorption) or cannot be combined with high-P cells (e.g. TEM)

Goal: Observe fluid behavior within the shale nanoporous matrix *in situ* at field-relevant pressures to optimize hydrocarbon production.

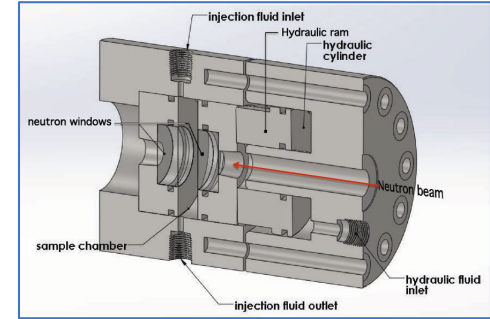


Theoretical shale production curve

Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

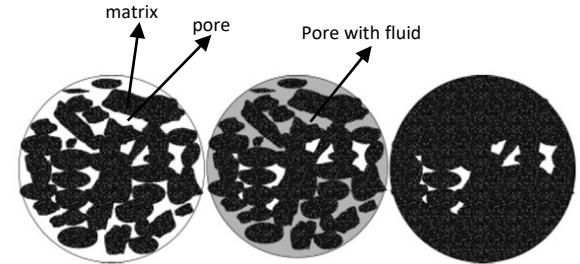
SANS experimental method

- Small-angle neutron scattering (SANS) is a powerful technique capable of measuring changes in 1 to 100 nm pores
- SANS measures the difference in scattering between a rock matrix and the pore space of a rock, i.e. the contrast
 - Adding/removing fluid from nanopores changes this contrast
- Large penetration depth of neutrons allows for combination with pressure cell



LANL-designed SANS compression cell

Hjelm et al., Rev Sci Instrum, 89, 055115 (2018)



Contrast matching technique

Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Water accessibility of clay- vs. carbonate rich shales

- Clay- and carbonate-rich shales of interest to industry partner collected from the Permian Basin
- Significant difference in organic matter content in addition to clay/carbonates.
- QXRD used to calculate SLDs for contrast-matching

Quantitative XRD

Sample ID	29Ha	43P
Quartz	52	4
Feldspars	8	3
Carbonates	2	91
Other (pyrite, fluorapatite, chlorite)	5	1
Organic Matter	5	0
Clays (>95% illite)	29	1
<i>OM + Clay</i>	34	1
Scattering Length Density (SLD)	3.81	4.67
% Deuterated Water	64%	76%

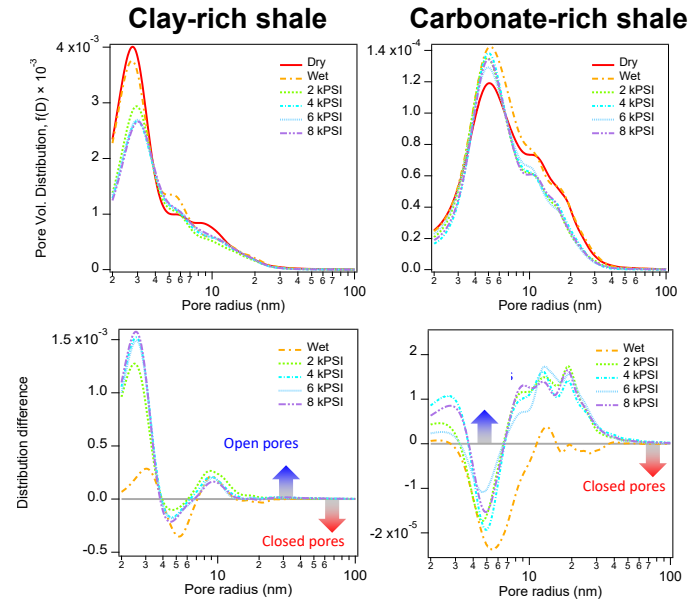
Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Water accessibility of clay- vs. carbonate rich shales

- Clay- and carbonate-rich shales were pressurized with contrast-matched water up to 8,000 psi
- Observed regions of closed and open porosity
 - 5 nm closed pores likely hosted by organic matter
 - Smaller wettable pores are intraparticle pores in clay minerals

Organic matter hosted pores not accessible to water-based fracking solutions, even at 8000 psi.

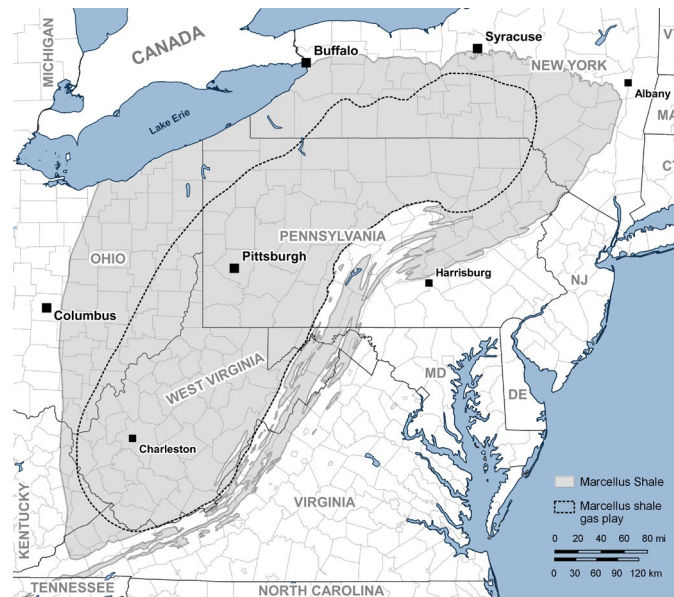
Pore size distributions from SANS



Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Methane recovery from Marcellus Shale

- In 2011, the USGS estimated that the Marcellus Shale formation contains 42.954 to 144.145 trillion cubic feet of undiscovered, technically recoverable natural gas
- Production increased from 5 Bcfpd in 2012 to more than 20 Bcfpd in 2018
- Interest in maximizing recoverability from this resource

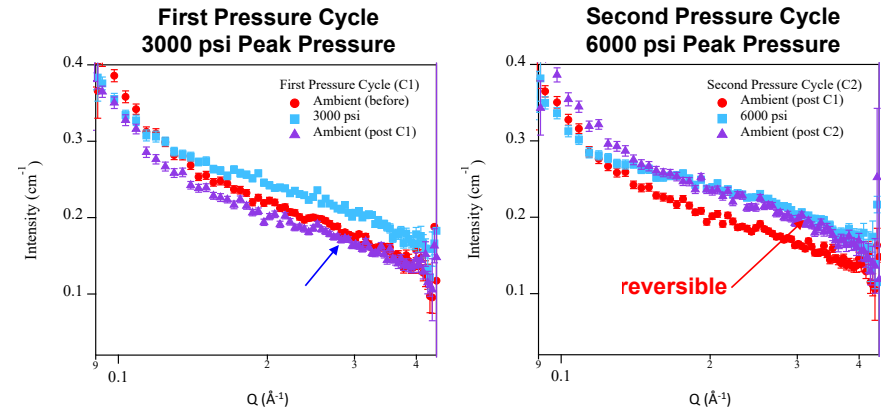


Marcellus Shale Gas Play

Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Methane trapping in small Marcellus Shale nanopores

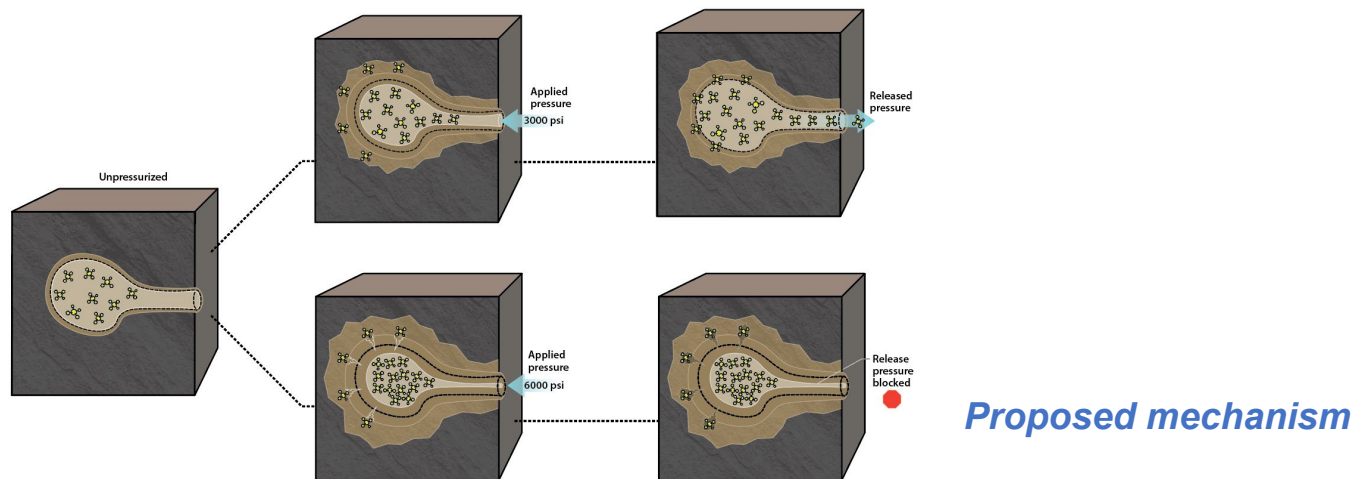
- Marcellus shale was put through two pressure cycles: one with a peak pressure of 3000 psi and one with a peak pressure of 6000 psi.
- Observed irreversible trapping of dense methane in small kerogen pores for 6000 psi cycle
 - Deformation of kerogen occurs at $P > 3000$ psi



*SANS high Q scattering profiles
correlate with small pore changes*

Characterizing fluid behavior in shale nanopores using small angle neutron scattering (SANS)

Methane trapping in small Marcellus Shale nanopores



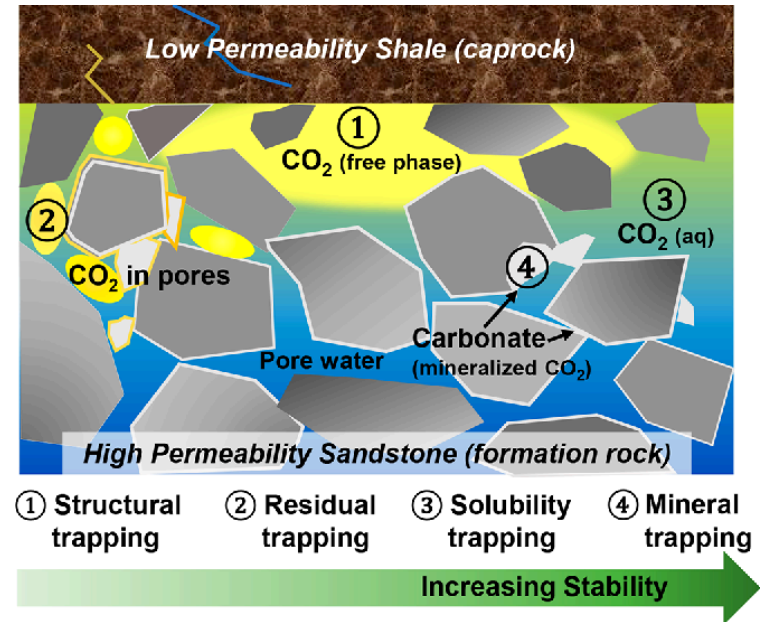
Pressure management is key for improving recovery—models must account for matrix nanopore effects!

Investigating geologic carbon sequestration (GCS) in mafic/ultramafic rocks

Background/Motivation

- Large capacity for CO₂ storage in subsurface formations, with the potential to revolutionize our approach to climate change mitigation
- Current strategies rely heavily on caprock integrity for storage safety post-injection
- Recently, pilot tests of CO₂ injection in basalt have shown rapid mineralization– 90% of injection CO₂ mineralized in 2 years!

Goal: Explore reaction conditions which promote CO₂ mineralization in mafic/ultramafic rock.

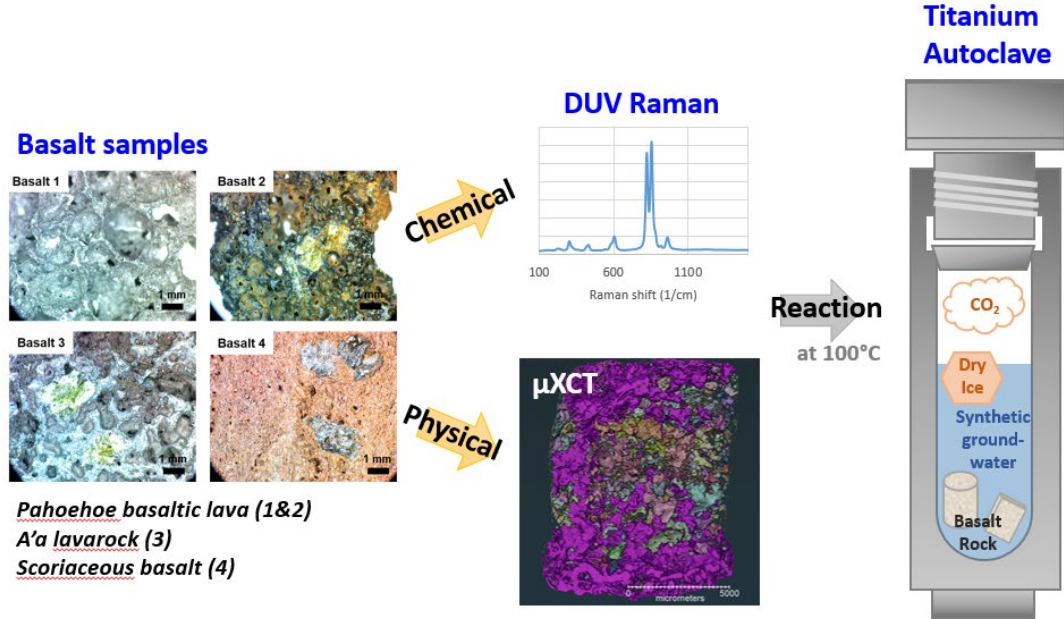


Trapping mechanisms for geologic carbon sequestration

Investigating geologic carbon sequestration (GCS) in mafic/ultramafic rocks

Ongoing experiments

- Thoroughly characterized geochemical differences and structure of four basaltic rocks
- Reacted in autoclaves under conditions to promote CO₂ mineralization
 - Dry ice – pressure
 - Oven at 100°C
- Recently finished reacting for 30 days, undergoing analysis for reaction extent (XCT, XRD, Raman)



Experimental plan for Basalt reactivity assessment

Earth Science Solutions for Global Security

- Measuring transport and reactivity of iodine through geologic media
- Understanding the diffusive transport of noble gas signatures in the subsurface

Measuring transport and reactivity of iodine through geologic media

Background/Motivation

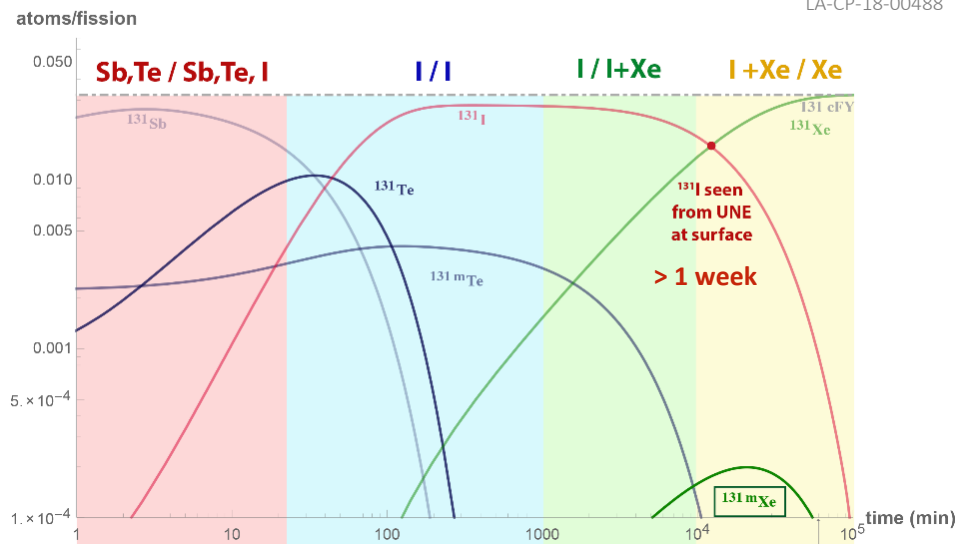
- Abundant radioxenon precursor, radioiodine, will be the dominant species during subsurface transport and has potential for redox reactions in subsurface
- Matrix diffusion of UNE fission products not well understood—a key retention mechanism

Goal: Matrix diffusion coefficients need to be constrained to improve modeling and event identification

131 Mass Chain Production

From ^{235}U Fission Source

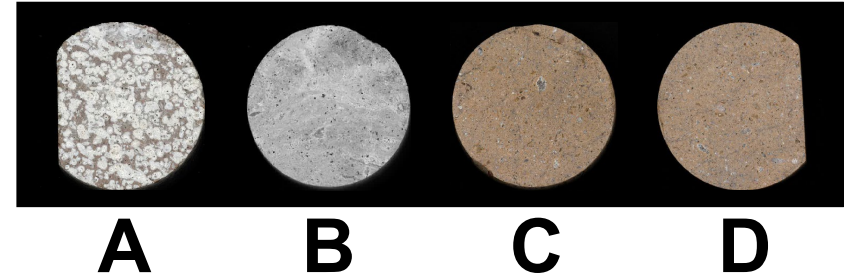
Brug, W.P.,
LA-CP-18-00488



Measuring transport and reactivity of iodine through geologic media

Iodine diffusion through geologic media

- Rock samples taken from Pahute Mesa at Nevada National Security Site (NNSS)
 - Previously characterized for diffusion using tritiated water

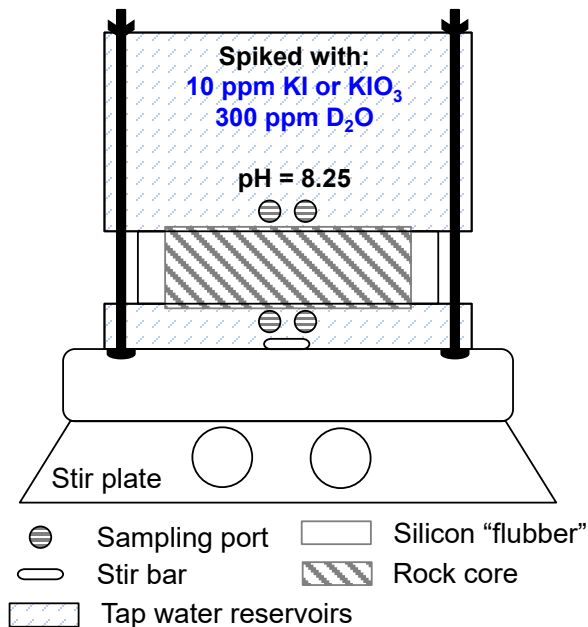


Core	Depth (ft bgs)	Hydrostratigraphic Unit	Rock Type	Area (cm)	Thickness (cm)	Porosity (ϕ)	Pore volume (cm ³)	Hydraulic conductivity (K, cm/sec)	Permeability (k, m ²)
A	1353-1353.28	Benham Aquifer	Lithophysae-rich lava flow	86.78	6.19	0.161	92.4	$2.68 \cdot 10^{-6}$	$2.74 \cdot 10^{-15}$
B	1925.1-1925.3	Benham Aquifer	Lithophysae-poor lava flow	43.92	5.54	0.143	35.3	$5.00 \cdot 10^{-7}$	$5.11 \cdot 10^{-16}$
C	2131.3-2131.5 (A)	Tiva Canyon Aquifer	Welded tuff	94.52	1.95	0.181	34.3	$1.47 \cdot 10^{-8}$	$1.50 \cdot 10^{-17}$
D	2131.3-2131.5 (B)	Tiva Canyon Aquifer	Welded tuff	87.85	3.06	0.179	49.5	$2.45 \cdot 10^{-8}$	$2.5 \cdot 10^{-17}$

Measuring transport and reactivity of iodine through geologic media

Experimental method

- Measured iodide (I^-)/ iodate (IO_3^-) diffusion through three types of rock
 - Lithophysae-rich lava flow (I^-), Lithophysae-rich lava flow (I^-), and two welded tuffs (I^- and IO_3^-)
- Cores saturated with deoxygenated tap water and placed in diffusion cell
 - Top chamber spiked with iodine species and conservative tracer (D_2O)
 - Samples taken from the bottom reservoir over 900+ hr
- Hydraulic conductivity re-measured after diffusion study



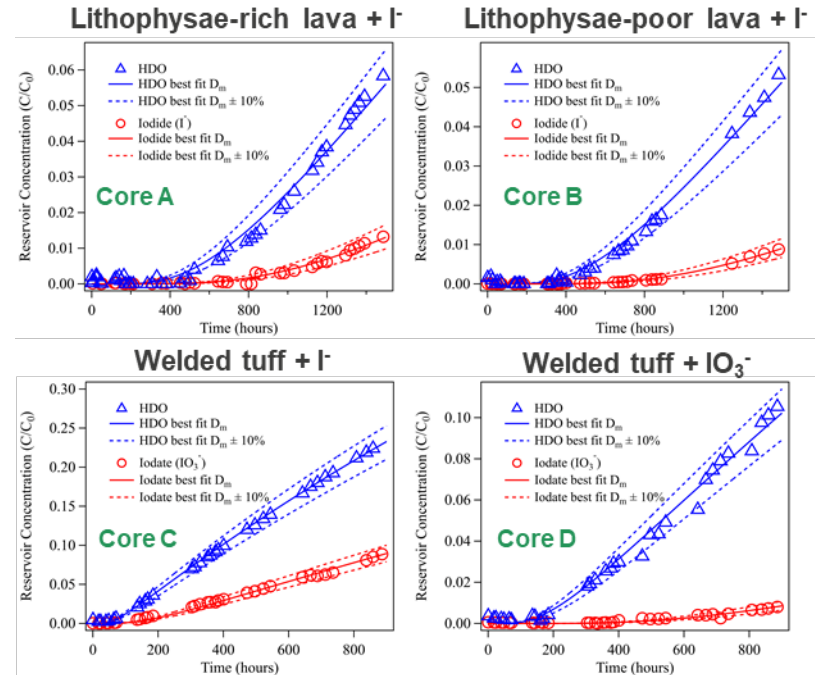
Diffusion cell apparatus

Measuring transport and reactivity of iodine through geologic media

Iodine diffusive transport results

- Aqueous iodine diffusion varies depending on rock type and iodine speciation (e.g., iodide vs. iodate)
 - Iodate diffusion slower than iodide through same rock type (welded tuff)
- Iodine diffusion slower than D_2O diffusion

Core	$D_m(D_2O)$ $\times 10^{-6} \text{ cm}^2/\text{s}$	$D_m(I^- \text{ or } IO_3^-)$ $\times 10^{-6} \text{ cm}^2/\text{s}$
A	2.29	1.15
B	2.07	0.9
C	2.43	0.98
D	2.03	0.49



Iodine breakthrough curves

Measuring transport and reactivity of iodine through geologic media

Iodine diffusive transport results

- Comparison of matrix with free water diffusion shows retardation due to anion/size exclusion
- Decreases in tracer diffusion for Cores B and D
 - Both also had decreases in hydraulic conductivity
 - Related to presence of iodate, as oxidation observed in Core B only

Anion & Size exclusion inhibit iodine transport

Rock Core	D_w/D_m for I	D_w/D_m for D_2O	Species	$D_w \times 10^{-6} \text{ cm}^2/\text{s}$
Core A (I^-)	17.7	10.0	D_2O	23.0
Core B (I^-)	22.7	11.1	I^-	20.4
Core C (I^-)	20.9	9.5	IO_3^-	14.3
Core D (IO_3^-)	28.9	11.3		

Iodine oxidation affects water matrix diffusion

Rock Core	$^3\text{HHO } D_m \text{ (cm}^2/\text{sec)}$	$D_2O \text{ } D_m \text{ (cm}^2/\text{sec)}$
Core A (I^-)	$2.30 \cdot 10^{-6}$	$2.29 \cdot 10^{-6}$
Core B (I^-)	$2.63 \cdot 10^{-6}$	$2.07 \cdot 10^{-6}$
Core C (I^-)	$2.4 \cdot 10^{-6}$	$2.43 \cdot 10^{-6}$
Core D (IO_3^-)	$2.5 \cdot 10^{-6}$	$2.03 \cdot 10^{-6}$

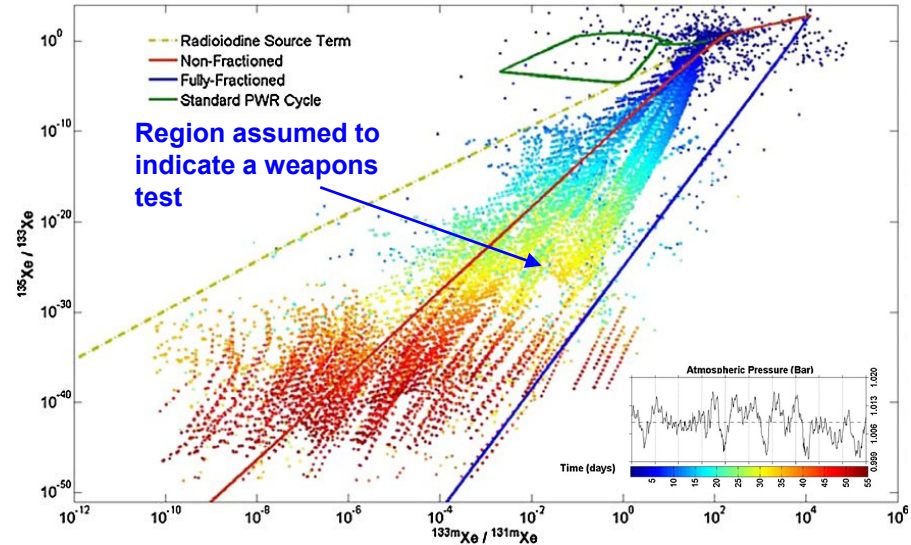
Understanding iodine speciation, reactivity is critical to predict transport.

Understanding the diffusive transport of noble gas signatures in the subsurface

Background/Motivation

- Noble gas fission products, such as xenon (Xe), are monitored to detect nuclear tests
- For well-contained subsurface tests, transport to the surface will impact detected isotopic ratios, complicating event identification

Goal: Improve understanding of the role of geochemical interactions and water saturation in subsurface gas diffusion



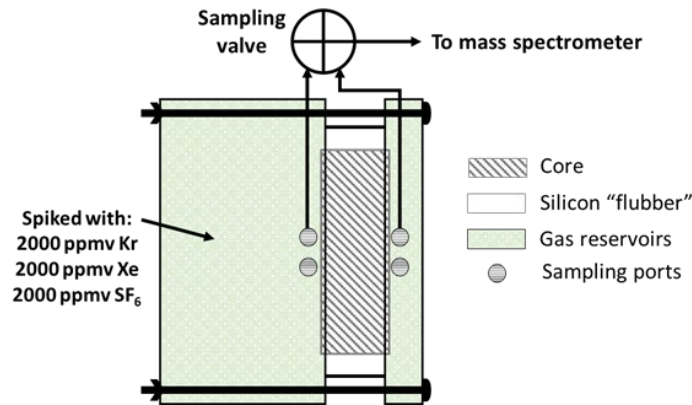
From Lowrey et al. *Geophysical Research Letters*, 40(1), (2013)

Four Xe isotope plot used for nuclear source attribution

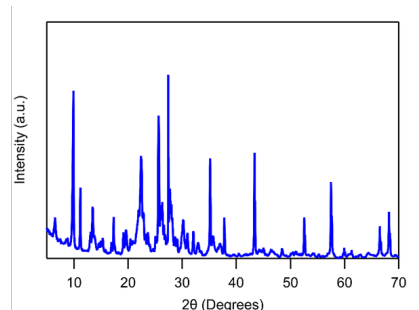
Understanding the diffusive transport of noble gas signatures in the subsurface

Experimental method

- Zeolitic nonwelded tuff taken from the Nevada National Security Site
- Core placed in diffusion cell
 - Larger reservoir spiked with gas mixture (krypton and xenon noble gases + sulfur hexafluoride, a commonly used tracer)
 - C_0 (spiked concentration) measured in large reservoir with mass spectrometer
- Valve measures C (breakthrough concentration) in the sampling reservoir every 10 minutes and C_0 every hour
- Diffusion measured on dry core and core saturated to 17%, 40%, 85% and 100% of total saturation



Gas diffusion cell apparatus



Zeolite	% of total mass
Heulandite	30.8
Mordenite	38.9
Analcime	2.1

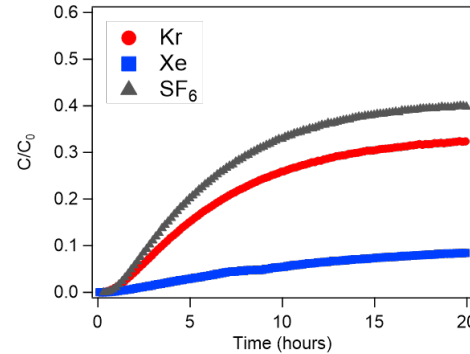
Understanding the diffusive transport of noble gas signatures in the subsurface

Gas transport results

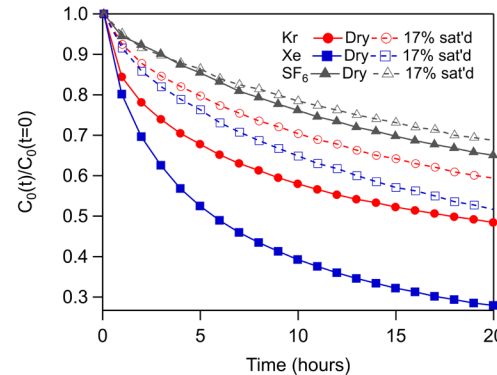
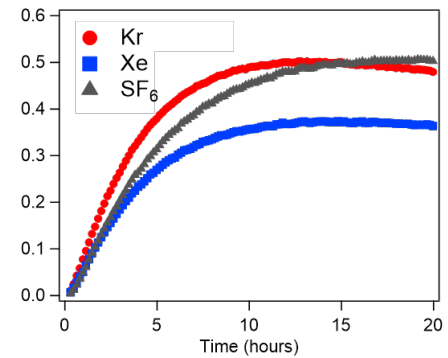
- For dry core, Xe diffusion through zeolitic tuff is much slower due to preferential sorption
 - Previously observed for natural zeolites
- Water inhibits sorption, resulting in faster breakthrough for all three gases in the 17% saturated system

Naturally-occurring zeolites impact transport due to sorption, and this degree is greatly impacted by saturation

Dry Rock Core



17% sat'd Core



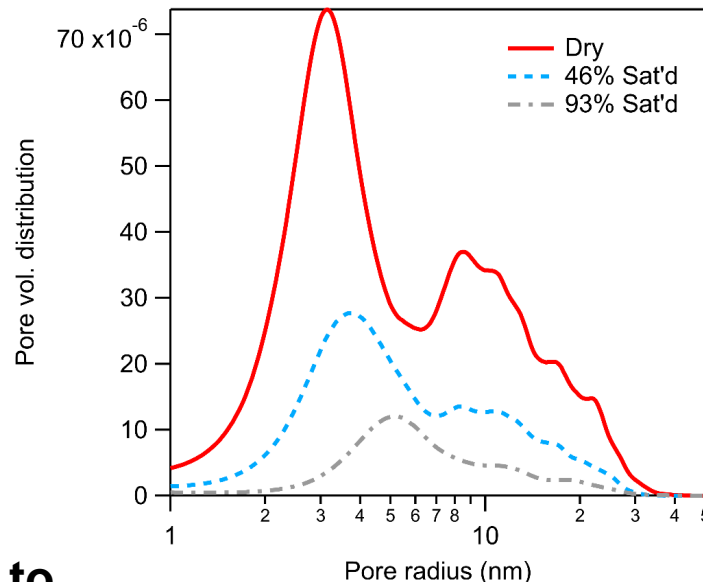
Breakthrough curves and C_0 changes for Kr/Xe/SF₆ diffusion through zeolitic tuff

Understanding the diffusive transport of noble gas signatures in the subsurface

Gas transport results

- Used SANS to study water interactions with rock nanopores
- Found that upon partial saturation, there was a dramatic decrease in the abundance of the smallest observable pore sizes
 - Size consistent with reported values for natural zeolites

Water fills zeolite pores, preventing gas sorption even at low saturations. Critical to include this phenomenon in fission product transport models.



SANS results for zeolitic tuff saturation

Conclusions

- Understanding and exploring geochemistry related to LANL's national and energy security missions is critical to meet program goals
- LANL has both the expertise and laboratory capabilities to conduct interesting and impactful geochemical studies



Acknowledgements

- Funding sources: LDRD, DOE-FE, Chevron, NNSA (NA-22)
- Collaborators:
 - Internal: Hongwu Xu, Rex Hjelm, Mohamed Mehana, Qinjun Kang, Hari Viswanathan, Hakim Boukhalfa, Pat Brug, Robert Roback, Doug Ware, Don Hickmott, Erik Watkins
 - External: Yimin Mao (NIST), Rebecca Stokes (Chevron), Tim Fischer (Chevron), Michael Cheshire (Chevron), Jon Burger (Chevron)

